A NEW TYPE OF COMPLEXOMETRIC TITRATION[1]

EARLE R. CALEY AND SABRI M. FARROHHA[2]
Department of Chemistry, The Ohio State University, Columbus 10

This method of titration depends on the equilibria relations that may exist in solution between a metal ion and an anion, which form, according to their concentrations, either an insoluble precipitate or a soluble complex ion of sufficiently low stability to decompose rapidly and reversibly on dilution. The solution of the metal ion is prepared for titration by adding a measured large excess of the anion in the form of a soluble salt, considerably more being added than is sufficient merely to redissolve the precipitate that is first formed. This prepared solution is titrated with distilled water up to the point where the soluble complex just begins to decompose as is indicated by the appearance of a slight turbidity due to the incipient separation of the insoluble precipitate formed between the metal ion and the anion. With other variables fixed, the volume of water required is a measure of the weight of metal ion present. This paper describes experiments with the silver iodide-iodide system, as a typical example, to determine whether this type of titration has any practical advantages.

TITRATION APPARATUS

The effect of temperature on volume of titrant required is much greater than in the usual type of titration. To avoid large corrections, titrations were performed at a standard temperature of 25 C. The titration vessel in the form of a lipless beaker was half immersed in a constant temperature bath, and was provided with a rubber stopper through which could be passed an electrically operated stirrer and the tip of the buret. The buret, with a capacity of 50 ml, was provided with an elongated offset tip and with a glass water jacket 4 cm in diameter which enveloped the buret from the stopcock to above the graduated portion. This jacket was connected to the constant temperature bath with rubber tubing so that the water of the bath could be constantly circulated through the jacket by an electric pump.

EXPERIMENTS

I. The first series of experiments was devised to estimate the minimum weights of ammonium iodide required to produce entirely clear solutions when added to silver nitrate solutions of various concentrations. A given weight of dried silver nitrate was weighed into a beaker and dissolved in a given volume of water delivered from a pipet. The beaker was then half immersed in the constant temperature bath maintained at 25 C. Dried ammonium iodide was added to the solution in successive weighed increments while the solution was being rapidly stirred. The first additions were relatively large, but as soon as the precipitated silver iodide showed signs of dissolving, the successive increments were sharply and progressively reduced, and the times of stirring were prolonged. Toward the end, the increments were in the range from 0.01 to 0.001 g. When the solution had lost its last trace of turbidity on thorough stirring, the weights of all the increments were added together to determine the total weight of ammonium iodide required. Representative results are shown in table 1. Since the results of duplicate trials often differed by as much as 0.01 g, these averaged results are given only through two decimal

[1]Part of a paper presented at the Sixty-ninth Annual Meeting of The Ohio Academy of Science, Antioch, Ohio, April 22, 1960.

[2]Present address: Department of Chemistry, College of Science, Baghdad, Republic of Iraq.

places. No greater accuracy was needed because the data were used merely as a guide to insure addition of excess weights of ammonium iodide in subsequent experiments.

II. In this series ammonium iodide in excess over that needed to dissolve the silver iodide was added to silver nitrate solutions of fixed concentration, and the resulting solutions were titrated with water to the point where silver iodide reprecipitated. Dried silver nitrate was weighed into the titration vessel and dissolved

TABLE 1

Minimum weight of ammonium iodide needed to form clear solution of iodide complex in silver nitrate solutions of different concentrations at 25 C

Ag present g	Initial volume of solution ml	NH_4I needed av. weight g
1.000	50.00	14.85
1.000	25.00	9.51
1.000	20.00	8.33
1.000	15.00	7.10
1.000	10.00	5.75
1.000	5.00	4.34
0.200	15.00	3.91
0.200	10.00	2.97
0.200	5.00	1.91
0.100	15.00	3.18
0.100	10.00	2.39
0.100	5.00	1.49

TABLE 2

Volume of water required for titration at 25 C of iodide complex formed by adding different weights of ammonium iodide to silver nitrate solutions containing 0.1000 g of silver

NH_4I added g	Volume of Ag solution ml	Water required ml	Volume of Ag solution ml	Water required ml
4.000	10.00	10.74	20.00	0.58
4.500	10.00	14.40	20.00	4.25
5.000	10.00	18.23	20.00	8.06
5.500	10.00	22.20	20.00	12.03
6.000	10.00	26.28	20.00	16.11
6.500	10.00	30.54	20.00	20.37
7.000	10.00	34.90	20.00	24.72

in a given volume of water delivered from a pipet. A given weight of dried ammonium iodide was then added and the solution was stirred until it reached the temperature of the bath. The titration was performed by the slow addition of water to the stirred solution until the first faint permanent turbidity appeared. Representative results are shown in table 2.

III. This series was similar to Series II except that parallel experiments were made at four different temperatures. The results in table 3 illustrate the effect of temperature. This effect is much larger than can be ascribed to changes in volume caused by temperature, and must be due largely to a decrease in the stability of the silver iodide-iodide complex with increase in temperature. Though the

figures in table 3 might seem to indicate that the changes in the volume of water required follow a simple regular pattern, an analysis of these figures shows that the effect is a complex one that cannot be corrected by a single temperature coefficient. It is better, therefore, to titrate at some standard temperature rather than to attempt to apply complex corrections. The results in table 3 show that for accurate results the temperature in titrations of this type should be held to within 0.1 C of the selected standard temperature.

IV. In this series the conditions simulated those for actual determinations of silver. In a given group of experiments a graded series of weights of dried silver nitrate were separately dissolved in identical volumes of water, and the same weight of dried ammonium iodide was added to each solution, which was brought to 25 C and titrated. Representative results are shown in table 4. The unusual feature of these results is that, contrary to any other type of titration, the volume of titrant increases with decrease in the weight of substance being titrated. This

TABLE 3

Volume of water required at different room temperatures for titration of iodide complex formed by adding different weights of ammonium iodide to 5.00 ml of silver nitrate nitrate solution containing 0.1000 g of silver

	Volume of water required at given temperature			
NH_4I added g	15 C ml	20 C ml	25 C ml	30 C ml
2.500	6.47	6.10	5.80	5.58
3.000	9.82	9.32	8.94	8.67
3.500	13.30	12.71	12.26	11.97
4.000	16.93	16.30	15.77	15.45
4.500	20.73	20.05	19.41	19.09
5.000	24.72	23.95	23.22	22.85
5.500	28.86	27.95	27.19	26.73
6.000	33.14	32.05	31.28	30.70

means that the absolute error of measurement should decrease as this weight decreases. Consequently, this type of titration should be especially advantageous for the accurate determination of very small weights of silver. However, it may also be used for the determination of larger amounts since the volume of titrant may be controlled by the proper selection of the volume of initial solution and the weight of ammonium iodide added. These results also show that the amount of silver to be determined should be known approximately beforehand. If entirely unknown, it may be rapidly estimated by adding test weights of ammonium iodide to aliquots of the unknown silver solution and titrating. The following is a detailed procedure for a silver solution estimated to contain between 0.00200 g and 0.01000 g of silver per ml.

PROCEDURE

By means of a micropipet or microburet, deliver a 5-ml aliquot of the silver solution into a 100-ml titration vessel for use with the apparatus already described. Add 4.000 g of ammonium iodide previously dried at 110 C, and when this has dissolved add 20.00 ml of water at 25 C from the jacketed buret. Stopper the vessel, half immerse it in the constant temperature bath maintained at 25 C, and stir slowly for about 30 minutes. Continue stirring and complete the titration by the slow addition of water until the first permanent turbidity appears. Find the

weight of silver corresponding to the total buret reading from a titration curve or table prepared by titrating by this same procedure a graded series of standard silver solutions having a range of concentration which includes that of the unknown.

Notes on Procedure.—If a buret or pipet of high precision is not available, it is better to weigh 5.000 g of the sample solution into the titrating vessel. The purpose of first adding a portion of the water required for the total titration is to provide sufficient volume for efficient stirring. The solution is stirred for the recommended

TABLE 4

Volume of water required for titration at 25 C of iodide complex formed by adding a fixed weight of ammonium iodide to a fixed volume of silver nitrate solution of varying concentration

NH_4I added g	Volume of solution ml	Ag content g	Water required ml	Ag per ml of water g
8.000	10.00	1.0000	8.90	0.1124
8.000	10.00	0.8000	12.15	0.0658
8.000	10.00	0.6000	16.09	0.0373
8.000	10.00	0.4000	21.68	0.0185
8.000	10.00	0.2000	31.71	0.00631
8.000	10.00	0.1000	43.43	0.00230
4.000	5.00	0.1000	15.70	0.00636
4.000	5.00	0.0800	17.76	0.00450
4.000	5.00	0.0600	20.35	0.00295
4.000	5.00	0.0400	24.38	0.00165
4.000	5.00	0.0200	33.75	0.00059
4.000	5.00	0.0100	48.36	0.00021
1.000	1.00	0.0100	6.24	0.00160
1.000	1.00	0.0080	6.85	0.00117
1.000	1.00	0.0060	7.73	0.00078
1.000	1.00	0.0040	9.48	0.00042
1.000	1.00	0.0020	15.79	0.00013
1.000	1.00	0.0010	22.50	0.00004

TABLE 5

Test determinations

Ag taken g	Standard titration reading ml	Sample titration reading ml	Difference in volume ml	Absolute error for Ag g
0.05000	22.07	22.13	+0.06	+0.00014
0.04000	24.36	24.40	+0.04	+0.00007
0.03000	27.67	27.63	−0.04	−0.00004
0.02000	33.79	33.70	−0.09	−0.00005
0.01000	48.40	48.32	−0.08	−0.00002

period in order to bring it to the temperature of the bath. Cross illumination of the solution during titration is helpful in obtaining sharp and reproducible end-points. Concentrations of ions other than silver should be similar in sample and standards. The solution should be approximately neutral but exact adjustment is not necessary because the ammonium iodide buffers the solution to the proper pH range. Metals that form insoluble iodides interfere.

RESULTS AND DISCUSSION

Results of a test of this procedure are shown in table 5. As these results indicate, and as other experiments have clearly shown, the precision tends to decrease appreciably with increase in volume of water required for titration, so that the relative error of measurement remains approximately the same for different weights of silver. The endpoint error caused by the volume of water needed to produce a noticeable turbidity increases with increase in volume of the final solution, but is normally less than 0.10 ml, and is in effect cancelled out when standards and unknown are titrated to identical turbidities. The volumetric error involved in measuring out the solutions and in reading the buret probably accounts for some of the observed inaccuracy. However, the absolute accuracy in the determination of these small amounts by this method exceeds that of the usual titration methods for silver. Experiments on a few other systems indicated that the principle of this method of titration may be applied to the accurate determination of small amounts of various metals.